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Synthesis and characterization of (η^5-C_5Me_5)$_2$TaCl(THF), a useful synthetic precursor for the preparation of oxo, imido and methylidene derivatives of permethyltantalocene *

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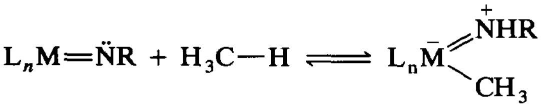
Abstract

The synthesis and characterization of $Cp^*_2Ta(=O)Cl$ ($Cp^* = (\eta^5$-$C_5Me_5)$), $Cp^*_2Ta(=NPh)Cl$, $Cp^*_2Ta(=O)H$, $Cp^*_2Ta(=NR)H$ (R = Ph, CMe_3), $Cp^*_2Ta(=CH_2)H$, $Cp^*_2Ta(=CH_2)Cl$, $Cp^*_2Ta(H_2C{=}CH_2)H$, and the unusual cyclometallated product $Cp^*(\eta^6$-$C_5Me_4CH_2)TaH_2$ from $Cp^*_2TaCl(THF)$ (THF = tetrahydrofuran) is described. $Cp^*_2TaCl(THF)$ is prepared by the Na/Hg reduction of $Cp^*_2TaCl_2$ in THF and used *in situ*. These synthetic routes are more convenient than those previously described and in most cases give much higher yields and purer products. All attempts to isolate $Cp^*_2TaCl(THF)$ as a pure crystalline solid have led instead to less reactive $[Cp^*_2TaCl]_n$, whose structure is uncertain. Although $Cp^*_2TaCl(THF)$ is only moderately stable in THF at room temperature, it has been characterized in solution by ^1H NMR spectroscopy. Both $[Cp^*_2TaCl]_n$ and $Cp^*_2TaCl(THF)$ react with CO to afford $Cp^*_2TaCl(CO)$. An X-ray crystal structure determination for $Cp^*_2Ta(=NPh)Cl$ (triclinic space group $P\bar{1}$ (number 2) with $Z = 2$; $a = 8.627(2)$; $b = 9.538(5)$, $c = 16.890(5)$ Å, $\alpha = 74.81(3)°$, $\beta = 87.12(2)°$, $\gamma = 63.79(3)°$, with $V = 1200.0(8)$ Å^3) reveals a linear Ta–N–C group, as had been found previously for the closely related complex $Cp^*_2Ta(=NPh)H$.

1. Introduction

Transition metal complexes having imido, oxo and alkylidene ligands are of continuing interest in organometallic chemistry [1]. Whereas alkylidene complexes commonly undergo reactions at the $[M{=}CR_2]$ functional group, oxo and imido derivatives normally have relatively inert spectator $[\overset{-}{M}{=}\overset{+}{O}]$ and $[\overset{-}{M}{=}\overset{+}{N}R]$ groups, triply bonded to the metal as four electron donors [2]. An increasing number of complexes having two electron, doubly-bonded oxo and imido ligands, *viz.* $[M{=}\ddot{O}]$ and $[M{=}\ddot{N}R]$, recently have been described [3]. The latter types are often highly reactive, and in some cases will even activate C–H bonds (eqn. (1)) [3b–d].



$$L_nM{=}\ddot{N}R + H_3C{-}H \rightleftharpoons L_n\overset{-}{M}\begin{matrix}\nearrow \overset{+}{N}HR \\ \searrow CH_3\end{matrix} \qquad (1)$$

Since the electrophilic character of the early transition metal centers is undoubtedly important to their high reactivity, we reasoned that cationic complexes of the type $[Cp^*_2Ta(=Y)]^+$ (Y = O, NR, CR_2) could be even more reactive than their isoelectronic neutral Zr analogs that activate benzene C–H bonds [3c]. In this article we describe our efforts to develop a general synthetic route to the neutral hydrides and chlorides $[Cp^*_2Ta(=Y)X]$ (X = Cl, H, Me; Y = O, NR, CR_2), which should function as precursors to these cations. Although $Cp^*_2Ta(=O)Cl$ [4] and $Cp^*_2Ta(=Y)H$ (Y = O), NR) [5] have been prepared previously, a more convenient, general route to these compounds is needed. $Cp^*_2Ta(=CH_2)H$ has been prepared previously by reaction of $Cp^*_2TaCl_2$ with 2.5 equivalents of CH_3Li [6]. Whereas this procedure provides acceptable yields (*ca.* 85%), we have found that even crystalline samples of $Cp^*_2Ta(=CH_2)H$ thusly prepared are commonly contaminated with variable amounts of

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* Dedicated to Mike Lappert on the occasion of his 65th birthday.

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$Cp^*_2Ta(=CH_2)CH_3$. This reaction likely proceeds via initial reduction of $Cp^*_2TaCl_2$ by methyllithium to a highly reactive Ta^{III} chloride, which subsequently undergoes metathesis followed by α-hydrogen elimination. $Cp^*_2Ta(=O)Cl$ and $Cp^*_2Ta(\eta^2\text{-}CH_2O)H$ are prepared by treatment of $Cp^*_2TaCl_2$ with Na/Hg in the presence of PhIO or $NaOCH_3$, respectively [6]. The procedure for $Cp^*_2Ta(=O)Cl$ has proven to be unreliable, and the yields are normally rather poor [4]. Since these reactions also likely involve reduction to the same Ta^{III} chloride species proposed above, we sought a method for its generation *in situ* as a first step for more general and convenient synthetic procedures to complexes of the type $[Cp^*_2Ta(=Y)X]$ (X = Cl, H, CH_3; Y = O, NR, CR_2). We report herein that reduction of $Cp^*_2TaCl_2$ with sodium amalgam in tetrahydrofuran cleanly affords moderately stable, yet highly reactive $Cp^*_2TaCl(THF)$.

2. Results and discussion

When a THF slurry of $Cp^*_2TaCl_2$ (**1**) is treated with one equivalent of Na/Hg over one hour at 25°C, a yellow-brown solution results. If this reaction is conducted in THF-d_8 the ^1H NMR spectrum displays a singlet a δ 1.96, which may be attributed to the Cp* methyl hydrogens of $Cp^*_2TaCl(THF)$ (**2**). Although we have not been able to isolate this complex, Green has isolated isostructural species of the type $Cp'_2TaCl(L)$ ($Cp' = C_5H_4(CHMe_2)$; L = PMe_3, CO) by the reduction of Cp'_2TaCl_2 with Mg/Hg in toluene in the presence of trimethylphosphine or carbon monoxide [7]. Analogous chloro-tetrahydrofuran adducts have been reported for the related permethylmetallocenes of cerium [8], samarium [9], neodymium [10], ytterbium [10], scandium [11], holmium [12], lutetium [13], yttrium [14], uranium [15], and titanium [16].

As expected on the basis of previous reports [17], treatment of solutions of **2** with N_2O leads to immediate formation of $Cp^*_2Ta(=O)Cl$ (**3**) with concomitant extrusion of N_2. Replacement of N_2O with other oxygen donors led to no reaction in the case of $Ph_3P{=}O$ [18]. The ^1H NMR spectrum for **3** in benzene-d_6 shows a singlet at δ 1.85 for the Cp* methyl hydrogens, and the ir spectrum displays a strong band at 850 cm^{-1} attributable to ν(Ta=O). This relatively low IR stretch is identical to that recorded previously for $Cp^*_2Ta(=O)H$ (**5**) indicative of a tantalum–oxygen bond order between two and three [5].

Treatment of a THF solution of **2** with PhN_3, a potent [NPh] donor which has been used previously in the synthesis of metal-imido complexes [19], leads to formation of a bright orange solution of $Cp^*_2Ta(N_3Ph)Cl$ which has been identified by its ^1H NMR spectrum (s, δ 1.83 ($\eta^5\text{-}C_5(CH_3)_5$)); d, δ 6.98 (*ortho* C_6H_5),

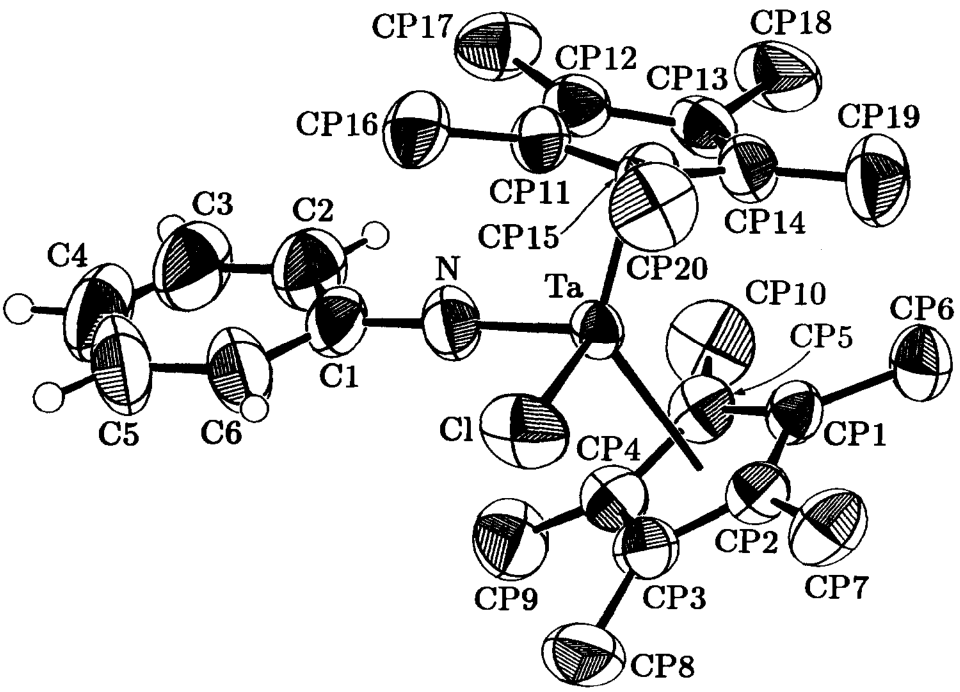


Fig. 1. ORTEP drawing of $Cp^*_2Ta(=NPh)Cl$ (**4**), with 50% probability ellipsoids. Hydrogen atoms on the phenyl ring are shown one-tenth size; those on methyl groups are not shown.

TABLE 1. Selected bond angles (°) for $Cp^*_2Ta(=NPh)Cl$ (**4**)

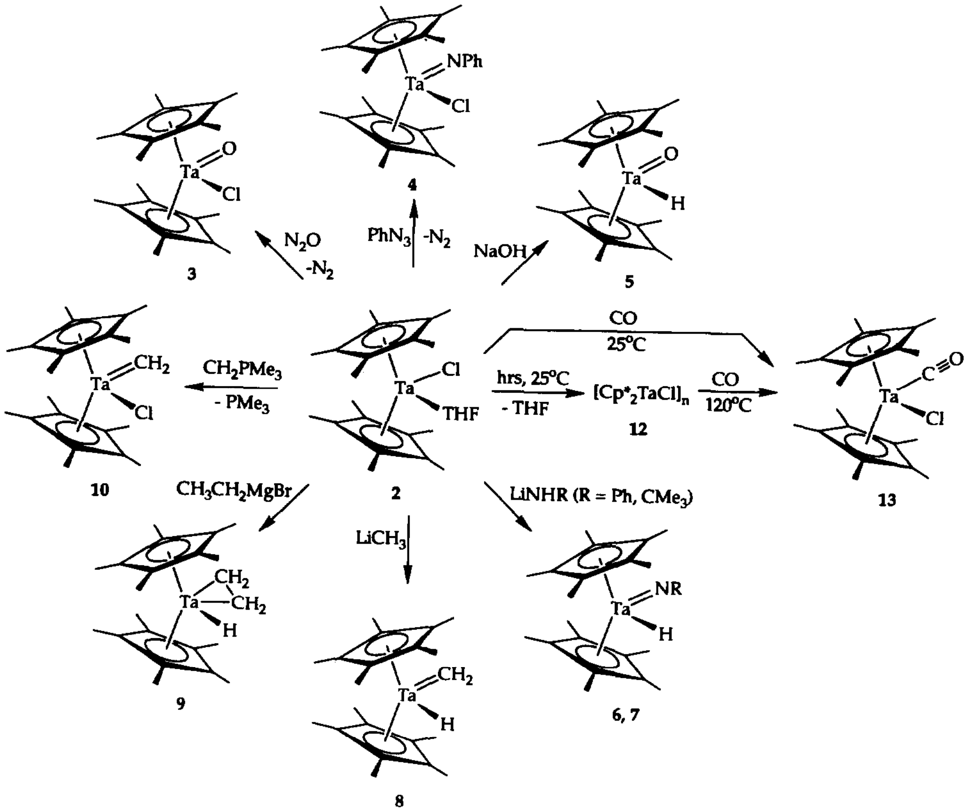
Cl-Ta-N	94.8 (1)
Cl-Ta-Cp1	102.8
Cl-Ta-Cp2	101.9
N-Ta-Cp1	108.1
N-Ta-Cp2	108.5
C1-N-Ta	176.4 (4)
C2-C1-N	123.0 (5)
C6-C1-N	118.8 (5)

TABLE 2. Selected bond distances (Å) for $Cp^*_2Ta(=NPh)Cl$ (**4**)

Ta-Cl	2.421 (1)
Ta-N	1.799 (4)
Ta-Cp1	2.196
Ta-Cp2	2.222
Ta-CP1	2.550 (4)
Ta-CP2	2.531 (5)
Ta-CP3	2.506 (5)
Ta-CP5	2.487 (5)
Ta-CP5	2.436 (5)
Ta-CP11	2.470 (5)
Ta-CP12	2.449 (5)
Ta-CP13	2.506 (5)
Ta-CP14	2.625 (5)
Ta-CP15	2.581 (5)
N-C1	1.376 (7)

t, δ 7.31 (*para* C_6H_5), *t*, δ 8.89 (*meta* C_6H_5)). Evaporation of the THF followed by heating for ten minutes in toluene yields $Cp^*_2Ta(=NPh)Cl$ (**4**) in 76% yield. The ^1H NMR spectrum for **4** is quite similar to that for $Cp^*_2Ta(N_3Ph)Cl$ (see experimental section). When $PhCH_2N_3$ is used as the [NR] donor, dinitrogen extrusion occurs at room temperature, as evidenced by instantaneous bubbling upon addition of the azide. Unfortunately, the presumed benzyl-imido complex is thermally unstable, and all attempts to purify it have led instead to decomposition to several products.

Orange crystals of **4** were grown by slow cooling to −78°C in diethyl ether and the X-ray crystal structure determined. Figure 1 shows the bent-metallocene structure of **4** and Tables 1–3 summarize the relevant crystal and structural data. As shown in Fig. 1, the phenyl imido ligand lies (38°) on one side of the plane defined by the Ta atom and the two Cp* centroids, while the chloride lies (57°) on the other side. These angles are similar to those reported for isostructural $Cp^*_2Ta(=NPh)H$ (**6**) [5], although the N–Ta–H angle (81.6°) is smaller than that for N–Ta–Cl (94.8(1)°), presumably due to the larger size of the Cl atom. The centroid–metal–centroid angle of 133.4° is as expected



Scheme 1.

TABLE 3. Crystallographic data for Cp$^*{}_2$Ta (=NPh)Cl

Formula	$TaC_{26}H_{35}ClN$
Fw	577.97
a (Å)	8.627 (2)
b (Å)	9.538 (5)
c (Å)	16.890 (5)
α (deg)	74.81 (3)
β (deg) 87.12 (2)	
γ (deg)	63.79 (3)
V (Å^3)	1200.0 (8)
Z	2
Space group	$P\bar{1}$
T (°C)	24
λ (Å)	0.71073
ρ_{calcd} (g cm^{-3})	1.60
μ (cm^{-1})	46.51
Transm coeff: max; min	1.169; 0.786
R [a]	0.037

[a] $R = (|\Sigma|F_o| - \Sigma|F_c||)/\Sigma|F_o|$ for all $F_o^2 > 0$.

for bent metallocenes of this type, as are the Ta-centroid distances of 2.196 and 2.222 Å.

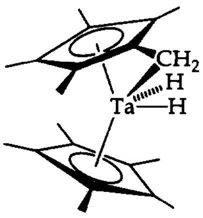
Another structural feature which is similar to that found for the analogous hydride is the nearly linear Ta–N–C_{ipso} angle: 177.8(9)° for **6** *vs.* 176.4(4)° for **4**. The Ta–N bond distance is 1.799(4) Å is comparable to that for the hydride **6** (1.831(10) Å) and slightly longer than those for $(Me_2N)_3Ta(NCMe_3)$ (1.77(2) Å) [20] and $(PEt_3)Cl(THF)_2Ta(NPh)$ (1.765(5) Å) [21], both of which may be considered as $[\overset{-}{\text{Ta}}\equiv\overset{+}{\text{N}}]$ triple bonds. As has been previously discussed, these longer Ta–N distances and the near linearity of the Ta–N–C_{ispo} angle reflect a tantalum-nitrogen bonding description that lies somewhere between a $[\overset{-}{\text{Ta}}\equiv\overset{+}{\text{N}}]$ triple bond and a $\text{Ta}{=}\ddot{\text{N}}$ double bond with a lone pair localized in a p orbital on nitrogen [5,22].

When solutions of **2** are treated with one equivalent of a concentrated aqueous solution of sodium hydroxide Cp$^*{}_2$Ta(=O)H (**5**) is formed, presumably *via* displacement of chloride by hydroxide followed by α-hydrogen elimination. This reaction proceeds in 86% isolated yield, and thus represents an improvement over the sequence that involves treatment of **1** with methyl lithium, isolation of Cp$^*{}_2$Ta(=CH_2)H, followed by addition of water to yield **5** [5].

This same synthetic strategy can be extended to the preparation of imido hydrides from **2** and the corresponding lithium amide. Thus, Cp$^*{}_2$Ta(=NPh)H (**6**) and Cp$^*{}_2$Ta(=$NCMe_3$)H (**7**) are readily prepared by treatment of **1** with lithium anilide and lithium *tert*-butylamide in isolated yields of 83% and 90%.

Treatment of solutions of **2** with one equivalent of CH_3Li results in the immediate, *clean* formation of Cp$^*{}_2$Ta(=CH_2)H (**8**), which may be isolated in 77% yield and free of contamination by Cp$^*{}_2$Ta(=CH_2)CH_3 that results when **8** is prepared by treatment of Cp$^*{}_2$TaCl_2 with two equivalents of methyllithium. The preparation of Cp$^*{}_2$Ta(H_2C=CH_2)H (**9**) [23] in 72% isolated yield *via* reaction of **2** with CH_3CH_2MgBr is comparable to the previous procedure of treatment of Cp$^*{}_2$TaCl_2 with two equivalents of ethylmagnesium bromide.

Treatment of a THF solution of **2** with one equivalent of $LiBEt_3H$ results in the formation of the unusual "tucked-in" complex Cp*(η^6-$C_5Me_4CH_2$)TaH_2 (**11**) in 67% yield. Complex **11** has been prepared previously by an alternative route involving the reaction of **1** with excess $LiNMe_2$ or $LiCMe_3$ [24]. The ^{1}H NMR spectrum for **11** shows the expected pattern and integrated intensities for the five independent Cp* methyl hydrogen environments of 5:1:1:1:1, and the inequivalent methylene hydrogens, which normally show up as an AB quartet in related complexes [25], appear as a broad multiplet centered at δ 3.78 (see experimental section). The hydrides appear as two doublets with ^2J(H–Ta–H) = 16 Hz. The four Cp* methyl resonances, the inequivalency of the methylene hydrogens, as well as the fact that there are two hydride signals, demonstrates that the hydrides are *cis* and that there is no mirror plane in the molecule.



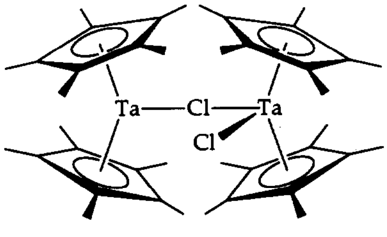
11

Formation of **11** can be envisioned as occurring *via* an oxidative addition of a ring methyl C–H bond to the electron rich d^2 metal center of [Cp$^*{}_2$TaH], which is generated by displacement of chloride from **2** by reaction with triethylborohydride.

Treatment of **2** with CH_2PMe_3, which has been used extensively as a methylene transfer reagent in related systems [26], affords Cp$^*{}_2$Ta(=CH_2)Cl (**10**) in 78% yield as a pale yellow solid. This compounds displays two singlets in the ^{1}H-NMR at δ 1.82 and 9.84 in a 15:1 ratio for the Cp* methyl and methylidene hydrogens, respectively.

All attempts to isolate **2** have failed. When solutions of **2** were filtered and tetrahydrofuran solvent removed, a red complex (**12**) which analyzes as [Cp$^*{}_2$TaCl]$_n$ was isolated in 88% yield. The same product was also obtained in the presence of PMe_3 or pyridine. Moreover, when solutions of **2** in THF-d_8 are allowed to stand at room temperature, peaks for complex **12** begin to appear in the ^1H NMR spectrum, and after *ca.* one day the conversion **2** to **12** is complete.

The ^1H NMR spectrum for **12** is puzzling, consisting of two equal intensity resonances at δ 1.88 and 1.96 attributable to two sets of inequivalent Cp*–methyl hydrogens. The ^{13}C NMR spectrum corroborates the presence of two types of Cp* ligands, displaying two types of ring carbons at δ 114.2 and 115.9 and two types of methyl carbons at δ 12.2 and 12.3. Suitable crystals for an X-ray structure determination could not be obtained, and the possibility of establishing the molecular weight was precluded by the fact that this compound decomposes slowly at room temperature over a matter a days. Related complexes include Cp^*_2VCl [27] and Cp^*_2TiCl [16], both of which exist as stable monomers, $[Cp^*_2UCl]_3$ [15] and $[Cp^*_2SmCl]_3$ [9], both of which exist as symmetrical trimers [15], $[Cp^*_2CeCl]_x$ [8], whose structure is believed to be polymeric, and $[Cp^*_2YCl]_2$ which exists as an unsymmetrical dimer with one terminal and one bridging chloride and the two Cp*(centroid)–metal–Cp*(centroid) planes perpendicular to one another [28]. The unsymmetrical nature of **12** based on the NMR data eliminates the former two structural possibilities, while the fact that $[Cp^*_2YCl]_2$ displays a ^1H NMR pattern of 2–1–1 for the Cp* methyl hydrogens argues against an analogous structure for **12**. Whereas we are unable to suggest an altogether satisfactory structure, we conclude that **12** is most likely a higher oligomer, like the cerium analog, or an unsymmetrical dimer in which the Cp*(centroid)–Ta–Cp* (centroid) planes are coincident. The latter structure is unprecedented and seems unlikely on the basis of steric arguments, however.



12 ???

Compound **12** cannot be converted back to **2** by heating in THF; however, it does react with CO, as does **2**, to form $Cp^*_2Ta(CO)Cl$ (**13**; $\nu(CO) = 1852$ cm^{-1}), but only with difficulty (120°C, 1 atm, 1 h). Furthermore, compound **12** does not react with N_2O or azides at room temperature, eliminating the possibility that **12** is the active species in the reactions for **2** reported above.

3. Conclusions

The tetrahydrofuran adduct of permethyltantalocene chloride, $Cp^*_2TaCl(THF)$, serves as a useful and convenient precursor to several derivatives of the type $Cp^*_2Ta(=Y)X$ ($Y = O$, NR, CH_2, CO; $X = Cl$, CH_3, H) in high yield. Its preparation by sodium amalgam reduction of $Cp^*_2TaCl_2$ in THF solution makes it readily available. As shown in the scheme, simple one step reactions provide a variety of complexes prepared previously as well as the new compound $Cp^*_2Ta(=CH_2)Cl$. In most cases, these represent superior synthetic routes. Attempts to isolate Cp^*_2TaCl-(THF), or related trimethylphosphine or pyridine adducts, have thus far been unsuccessful. Although $Cp^*_2TaCl(THF)$ decomposes to less reactive $[Cp^*_2TaCl]_n$, it does exhibit sufficient thermal stability to be used *in situ*.

4. Experimental section

All manipulations were performed on a conventional vacuum line by using standard Schlenk or cannula techniques or in a dry box under an atmosphere of dinitrogen. Solvents were dried by prolonged reflux over sodium benzophenone ketyl, followed by distillation under an atmosphere of dinitrogen. Ether solvents were stored over sodium benzophenone ketyl, and hydrocarbon solvents were stored over titanocene and vacuum transferred before use. $Cp^*_2TaCl_2$ was prepared according to the literature procedure [23]. Benzyl azide was obtained from Frinton Laboratories, dried over 4 Å molecular sieves and distilled under reduced pressure before use. Phenyl azide was prepared according to the literature procedure [29], distilled under reduced pressure and then dried over 4 Å molecular sieves before use. Lithium amides were prepared by deprotonation of the corresponding amine by n-butyllithium in petroleum ether. Trimethylphosphine, tetramethylphosphonium chloride, n-butyllithium (1.6 M in hexanes) methyllithium (1.4 M solution in diethyl ether), methyl magnesium bromide (3.0 M solution in diethyl ether), lithium triethylborohydride (1.0 M in tetrahydrofuran), and N_2O were used as received from Aldrich. Elemental analyses were provided by the Caltech microanalytical service. ^1H and ^{13}C nuclear magnetic resonance spectra were recorded on a GE 300 spectrometer in benzene-d_6 or THF-d_8 at ambient temperature. Infrared spectra were recorded on a Beckman 4240 spectrometer as Nujol mulls. Relative intensities are abbreviated as follows: vs (very strong), s (strong), m (medium), w (weak), bd (broad), sh (shoulder).

4.1. *Structure determination of $Cp^*_2Ta(=NPh)Cl$ (4)*

A single crystal needle was cut in half and sealed in a capillary under nitrogen. Altogether, 5493 independent reflections were collected over a range of 2θ of 1–27.5° on a CAD4 diffractometer. Cell dimensions were determined from the setting angles of 25 reflections with $15 > 2\theta > 19°$. The data were corrected for absorption and a slight decay and adjusted by Lorenz and polarization factors. Space group $P\bar{1}$ as chosen on the basis of two independent molecules in the unit cell; see Table 3 for crystallographic data. The Ta atom coordinates were found from a Patterson map and remaining heavy atoms were located by successive structure factor calculations and Fourier maps. All non-hydrogen atoms were refined by full-matrix least-squares methods with anisotropic thermal parameters. The phenyl hydrogen atoms, placed at calculated positions and the methyl hydrogen atoms, placed in idealized positions based on difference maps calculated in their expected planes, were included as fixed contributions to the structure factors. Several cycles of full-matrix least-squares refinement led to convergence with $R = 0.029$ for $F_o^2 > 3\sigma(F_o^2)$ (4627 reflections) and $R = 0.037$ for $F_o^2 > 0$ (5293 reflections). The final goodness of fit $([\Sigma w(F_o^2 - F_c^2)/(n-p)]^{1/2})$ is 1.57 for 5493 data and 263 parameters.

4.2. *Cp*$^*_2$*TaCl(THF) (2)*

THF solutions of **2** were generated by the reduction of $Cp^*_2TaCl_2$ (**1**) by Na/Hg in THF. In a typical preparation, **1** (500 mg, 0.957 mmol) was placed in a flask with freshly prepared Na/Hg (22 mg, 0.957 mmol Na in 1.0 ml Hg). THF (50 ml) was then added by cannula and the mixture stirred for *ca.* 1 h. Over this period the mixture changes from a green-brown slurry to a yellow-brown solution with a NaCl precipitate. This solution was then used directly in subsequent reactions.

4.3. *Cp*$^*_2$*Ta(=O)Cl (3)*

N_2O was bubbled vigorously through a solution of **2** (0.957 mmol) in THF (50 ml). The solution rapidly faded from deep yellow-brown to light yellow over 5 min. After 30 min further stirring, the solution was filtered and the THF removed *in vacuo*. The pale solid was then extracted into toluene and filtered to give a pale-yellow solution. Concentration of this solution followed by addition of excess petroleum ether led to the precipitation of a fawn solid which was collected by filtration, washed with 3 × 10 ml petroleum ether, and dried overnight *in vacuo* to give 375 mg (78% yield) of **3**. Anal. Calcd for $C_{20}H_{30}ClOTa$: C, 47.77; H, 6.01. Found: C, 47.65; H, 5.86. ^{1}H NMR(benzene-d_6): δ 1.85 [s, $C_5(CH_3)_5$]. IR (Nujol, cm^{-1}) 850 (s) ν(Ta=O).

4.4. *Cp*$^*_2$*Ta(=NPh)Cl (4)*

To a solution of **2** (0.957 mmol) in THF (50 ml) was added by syringe PhN_3 (0.104 ml, 0.957 mmol). The color rapidly changed from deep yellow-brown to light orange-yellow. The solution was then stirred for an additional 30 min, after which time it was filtered and solvent was removed *in vacuo* from the filtrate to dryness. The orange solid was then extracted into toluene, heated for 10 min to 90°C, cooled and subsequently filtered to give a yellow-orange solution. The toluene was then removed *in vacuo*, and the resulting solid extracted into a minimum volume of diethyl ether. This solution was slowly cooled overnight to give 420 mg (76% yield) of **4** as light orange crystals. Anal. Calcd for $C_{26}H_{35}ClNTa$: C, 54.03; H, 6.10; N, 2.42. Found: C, 53,80; H, 6.05; N, 1.95. ^{1}H NMR(benzene-d_6); δ 1.84 [s, $C_5(CH_3)_5$], 6.578 [d, ^3J(H–H) = 7.6 Hz, ortho C_6H_5], 6.60 [t, ^3J(H–H) = 7.6 Hz, *para* C_6H_5], 7.18 [t, ^3J(H–H) = 7.6 Hz, *meta* C_6H_5].

4.5. *Cp*$^*_2$*Ta(=O)H (5)*

Sodium hydroxide (96 μl of a 10 M aqueous solution) was added by syringe to a solution of **2** (0.957 mmol) in THF (50 ml). The color faded from deep yellow-brown to pale yellow over 5 min, and the resulting solution was stirred for an additional 30 min. This solution was then filtered, and the solvent removed *in vacuo*. The resulting pale solid was then extracted into toluene and the yellow solution filtered. Removal of the toluene *in vacuo*, followed by sublimation of the orange-brown residue at 10^{-6} Torr afforded pure **5** (385 mg, 86% yield). Spectroscopic data are as reported elsewhere [5].

4.6. *Cp*$^*_2$*Ta(=NPh)H (6)*

Lithium anilide (95 mg, 0.957 mol) was added by syringe to a solution of **2** (0.957 mol) in THF (50 ml), causing the solution to immediately change color from deep yellow-brown to yellow. The solution was then stirred for an additional 30 min, after which time it was filtered and the THF removed *in vacuo*. The resulting yellow residue was then extracted into pentane and filtered. Slow cooling to −78°C followed by filtration and drying *in vacuo* yielded 435 mg (83%) of **6** as a pale yellow solid. Spectroscopic data as reported elsewhere [5].

4.7. *Cp*$^*_2$*Ta(=NCMe*$_3$*)H (7)*

Following the procedure outlined above for the preparation of **6**, lithium tert-butyl amide (74.7 mg, 0.957 mmol) in THF (10 ml) was added by syringe to a solution of **2** (0.957 mmol) in THF (50 ml). Sublimation at 10^{-6} Torr gave 450 mg (90% yield) of **7**. Anal. Calcd for $C_{24}H_{40}NTa$: C, 55.06; H, 7.70; N, 2.68. Found: C, 54.87; H, 7.45; N, 2.31. ^{1}H-NMR (benzene-d_6); δ 1.32 (s, $C(CH_3)_3$), 2.01 (s, $C_5(CH_3)_5$), 6.85 (s, Ta–H).

4.8. $Cp^*{}_2Ta(=CH_2)H$ (8)

A 1.4 M solution of CH_3Li (684 μl, 0.957 mmol) was added by syringe to a solution of **2** (0.957 mmol) in THF (50 ml). The solution rapidly changed color from deep yellow-brown to pale yellow. The solution was then stirred for an additional 30 min and subsequently filtered. Evaporation of the THF *in vacuo* gave a pale residue which was then extracted into toluene. Concentration of this solution followed by addition of pentane and filtration of the pale precipitate gave 345 mg of pure **8** (77% yield). Spectroscopic data are as reported elsewhere [6].

4.9. $Cp^*{}_2Ta(H_2C=CH_2)H$ (9)

A 3.0 M solution of CH_3CH_2MgBr in diethyl ether (320 μl, 0.957 mmol) was added by syringe to a solution of **2** (0.957 mmol) in THF (50 ml). The solution changed color from deep yellow-brown to dark yellow over 5 min. After 30 min additional stirring the solution was filtered and the THF removed *in vacuo* to give a pale solid. Extraction into hot heptane followed by slow cooling to −78°C yielded 333 mg (72%) of **9** as a yellow solid. Spectroscopic data are as reported elsewhere [21].

4.10. $Cp^*{}_2Ta(=CH_2)Cl$ (10)

2 (0.957 mmol) in THF (50 ml) was treated with CH_2PMe_3 (0.957 mmol) in diethyl ether (30 ml). The solution changed color rapidly from deep yellow-brown to orange over 10 min and was then stirred for an additional 2 h. Filtration followed by removal of the THF *in vacuo* gave an orange residue which was subsequently extracted into toluene and filtered. The solution was then concentrated to *ca.* 2 ml and pentane (20 ml) was then added. The resulting precipitate was then collected and washed with 3 × 10 ml pentane. Drying *in vacuo* yielded 376 mg (78%) of **10** as a pale solid. Anal. Calcd for $C_{21}H_{32}ClTa$: C, 50.36; H, 6.44. Found: C, 49.42; H, 5.93. ^{1}H-NMR: δ 1.82 (s, $C_5(CH_3)_5$), 9.84 (s, $Ta{=}CH_2$).

4.11. $Cp^*(\eta^6\text{-}C_5Me_4CH_2)TaH_2$ (11)

To a solution of **2** (0.957 mmol) in THF (50 ml) was added 1.0 M $LiBEt_3H$ (0.957 ml, 0.957 mmol). The color rapidly faded from deep yellow-brown to orange over 5 min and the solution was stirred for an additional 2 h. Filtration followed by reduction of solvent volume and extraction of the orange residue into pentane yielded a pale yellow solution. Filtration of this new solution followed by concentration and slow cooling to −78°C yielded pale yellow crystals of **11** (299 mg, 67%). Anal. Calcd for $C_{20}H_{31}Ta$: C, 53.1; H, 6.9. Found: C, 52.7; H, 6.9. ^{1}H-NMR: δ 0.22 (d, ^2J(H–H) = 16 Hz, Ta–H_a), 0.73 (d, ^2J(H–H) = 16 Hz, Ta–H_b), 1.61 (s, CH_3), 1.62 (s, CH_3), 1.92 (s, $C_5(CH_3)_5$), 1.99 (d, ^4J(H–H) = 1.5, CH_3), 2.22 (d, ^4J(H–H) = 1.5, CH_3), 3.78 (m, CH_2).

4.12. $[Cp^*{}_2TaCl]_n$ (12)

A solution of **2** (0.957 mmol) in THF (50 ml) was stirred for three hours and then filtered, and the THF removed *in vacuo*. The red residue was then extracted into ether, filtered, and cooled to −78°C overnight. The resulting red needles of **12** were then collected by filtration, washed with 3 × 10 ml of pentane, and dried *in vacuo*. Yield = 410 mg (88%). Anal. Calcd for $C_{20}H_{30}ClTa$: C, 49.34; H, 6.21. Found: C, 49.01; H, 6.07. ^{1}H-NMR; δ 1.88 (s, $C_5(CH_3)_5$), 1.96 (s, $C_5(CH_3)_5$). ^{13}C-NMR (benzene-d_6) δ 12.2 (s, $(CH_3)_5$), 12.34 (s, $(CH_3)_5$), 114.2 (s, C_5), 115.9 (s, C_5).

4.13. $Cp^*{}_2Ta(CO)Cl$ (13)

A solution of **2** (0.957 mmol) in THF (50 ml) was stirred under one atmosphere of CO for *ca.* 2 h. The resulting emerald solution was then filtered and the THF removed *in vacuo*. Recrystallization of the dark green residue from THF/pentane yielded green crystals of **13**. Yield = 410 mg (83%). Anal. Calcd for $C_{21}H_{30}ClOTa$: C, 38.99; H, 5.87. Found: C, 48.64; H, 5.77. ^{1}H-NMR (benzene-d_6): δ 1.68 (s, $C_5(CH_3)_5$). IR (Nujol mull, cm^{-1}): 1852 (m) ν(CO).

5. Supplementary material available

A table of final parameters for the structure of $Cp^*{}_2Ta(=NPh)Cl$, assigned hydrogen parameters, anisotropic displacement parameters, complete distances and angles, and tables of observed and calculated structure factors have been deposited at the Cambridge Crystallographic Data Centre.

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